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PROVISIONAL APPLICATION COVER SHEET

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Sir:

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c):

Atty Docket Number: 11663-012

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TITLE OF INVENTION (280 characters max)

ANTI-GRIFITTI FORMULATION FOR POLYMER COMPONENTS

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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification: 8 pages	☒ Small Entity Assertion
☐ Drawing(s): _____ sheets	☐ Other (specify): _____

METHOD OF PAYMENT (check one)

☒ A check or money order is enclosed to cover the filing fee. ☐ The Director is hereby authorized to charge the filing fee to Deposit Account Number **23-1925**	PROVISIONAL FILING FEE AMOUNT(S)	$80.00

Was the invention made by, or under a contract with, an Agency of the United States Government?

☒ No.
☐ Yes. U.S. government agency: _____; Government Contract No.:_____.

Respectfully submitted,

February 19, 2004
Date

Raymond J. Vivacqua (Reg. No. 45,369)
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CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8

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APPLICATION FOR UNITED STATES LETTERS PATENT

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ANTI-GRIFITTI FORMULATION FOR POLYMER COMPONENTS

TECHNICAL FIELD

[0001] This invention generally relates to an anti-graffiti composition for a polymeric article.

BACKGROUND OF THE INVENTION

[0002] Today, more and more articles are being manufactured using polyolefin. Such polymeric products exhibit high resistance to breakage, scratch, temperature resistance etc. However, products made from polyolefin are very susceptible to marking using ink, paint etc. It is also very difficult to remove such markings from the surface of such articles.

[0003] Graffiti is a common problem encountered in areas of access to the general public for example, walls of a public restroom or portable restrooms or in a subway station. Moreover, generally, unwanted markings on surfaces can occur almost anywhere. Graffiti is often in the form of paint, such as spray paint, but graffiti and other markings may be applied by markers, crayons, and other writing fluids. As used herein, the term "graffiti" will be used to refer broadly to unwanted markings, whether consisting of paint, such other fluids or other unwanted markings, scuff marks and the like.

[0004] Such markings are particularly troublesome because they are often very difficult to remove from the surfaces on which they have been applied. Thus, painted surfaces often must be repainted to cover up the markings and sometimes must be even stripped and then repainted. For example, graffiti often is applied with paint similar to that on the surface. Removal of the graffiti paint by abrasion or with a solvent therefore is impractical because it typically results in removal of at least a

portion of the underlying paint. Unpainted surfaces sometimes must be sandblasted to remove the markings.

[0005] Other solutions also include coating the surface of the article that would serve as a barrier to permit easy removal of such markings. Or coating the surface that may be resistant to graffiti. However, such solutions are expensive and labor intensive. Additionally not all surfaces can be coated with graffiti-resistant coating.

[0006] Therefore, there is a need to have a new anti-graffiti composition which is resistant to graffiti.

DESCRIPTION

[0007] The following description of embodiments of the invention is not intended to limit the invention to these embodiments, but rather to enable any person skilled in the art to make and use this invention.

Tests were conducted in which Microcrystalline wax (#4) and Ultraflex amber Microwax (#5) were added to a polymer in addition to mineral oil in two different formulations. The details of the final formulation are shown in table below.

[0008]

Formulation #	% HDPE	% Mineral Oil	%Wax	Wax Type
1	99	1	0	None
2	98.7	1	0.3	#4
3	98.3	1	0.7	#4
4	98	1	1	#4
5	98.7	1	0.3	#5
6	98.3	1	0.7	#5
7	98	1	1	#5

[0009] In extruded sheet, all seven formulations passed the anti-graffiti test as described later. In thermoformed parts, formulation #4 was found to be better than #3, which was found to be better than #2, which was found to be better than #1 having no wax in the formulation. Similarly, in thermoformed parts, formulation #7 was found to be better than #6, which was found to be better than #5, which was found to be better than #1 having no wax in the formulation.

Conclusion: Increasing wax concentration in HDPE provides better anti-graffiti property.

[0010] In another experiment, the surface of the thermoforming mold was coated with a 50:50 mixture of mineral oil and candle wax. Extruded sheets produced from formulation # 1 through 7 were thermoformed. All seven products passed anti-graffiti test.

[0011] Conclusion: Applying a coating of 50:50 (wt.) mineral oil: candle wax on the mold surface provides anti-graffiti property to the part.

[0012] In another experiment, the extruded sheet of formulation #1 was wrapped with commercially available polyester sheet. The wrapped sheet was heated in the thermoforming oven and subsequently thermoformed. The part passed anti-graffiti test.

[0013] Conclusion: The polyester wrapping prevented the volatilization of the additive and hence anti-graffiti property was retained.

[0014] I. Compounding:

[0015] A 10 weight percent mineral oil in HDPE master batch, which will be identified as MB1, was produced in the first phase of the project. The second and third master batches containing mineral oil and each of the two waxes (#4 & #5) in HDPE were produced using a 34 mm diameter co-rotating twin screw extruder. Since the waxes are solid at room temperature, waxes were melt mixed with mineral oil at a 50:50 (wt.) ratio before compounding with the HDPE. The percent additive in the master batch was calculated to be 13% and was calculated using simple material balance equations. These master batches were identified as MB2 and MB3 containing additive #4 & #5 respectively. MB1, MB2 and MB3 were produced in pellet form so that they can be dry blended with virgin HDPE at any desired ratio.

[0016] II. Sheet Extrusion:

[0017] A 10" wide sheet die was used with a 1.25" diameter single screw extruder to produce 40mil thick 10" wide sheet. 12" diameter three stack chilled rolls were used as takeoff. Attempt was made to polish both sides of the extruded sheet. Extruder hopper was fed with MB1, MB2 and MB3 dry mixed with virgin HDPE. Table 1 shows the feed composition. The percent composition is shown in table 2.

[0018] Table 1 Pounds of HDPE, MB1, MB2 and MB3 used in various runs

Run#	HDPE	MB1	MB2	MB3
1	9	1	-	-
2	8	0.7	0.4	-
3	8	0.3	1	-
4	8	-	1.5	-
5	8	0.7	-	0.4
6	8	0.3	-	1
7	8	-	-	1.5

[0019] Table 2 Compositions by percent

Run#	% HDPE	% Mineral Oil	%Wax	Wax Type
1	99	1	0	None
2	98.7	1	0.3	4
3	98.3	1	0.7	4
4	98	1	1	4
5	98.7	1	0.3	5
6	98.3	1	0.7	5
7	98	1	1	5

[0020] III. Weight Loss Experiments:

[0021] In this part of the experiment an attempt was made to quantify the additive loss during heating of the sheet before thermoforming. 24" long extruded sheets were pre-weighed and heated inside a thermoforming oven, which was heated to 750F, for 40 sec. Then the sheet was allowed to cool down to room temperature and the sheets were weighed and percent weight loss was calculated. Same experiment was repeated for 35 and 45 sec. sheet heating time, and also at 700F oven temperature. Unfortunately, the result was not found to be conclusive.

[0022] IV. Anti-graffiti test on the Sheets:

[0023] The following markers were tested on the sheet.

[0024] 1. Pentel Permanent Markathon –Medium line – Chisel Tip (Black)

[0025] 2. Avery Marks-A-Lot Permanent (Blue)

[0026] 3. Avery Marks-A-Lot Permanent (Red)

[0027] Avery Marks-A-Lot Permanent (Black)

[0028] Sanford Deluxe Permanent Marker (Red)

[0029] Sanford Rub-a-Dub Laundry Marker (Black)

[0030] Sanford Sharpie Fine Point Permanent Marker (Black)

[0031] Sanford Sharpie Fine Point Permanent Marker (Blue)

[0032] The same test procedure that was developed in the earlier phase was followed. All the sheets passed the test.

[0033] V. Thermoforming:

[0034] A batch thermoformer was used for converting the sheet. A meat tray mold constructed of aluminum was used. The surface of the mold was glass beaten and Teflon coated. The mold temperature was maintained at 140F by circulation of hot water. The oven temperature was maintained at 750F. Oven heating time of 40 sec was used for all the sheets (Run #1 through #7 in Tables 1 & 2). Plug assisted vacuum was used for forming.

[0035] For each of the seven sheet formulations (Table 1 and Table 2), thermoformed parts were produced using two different methods. In one case, the mold surface was not treated. In the second case, the mold surface was coated with a 50:50 mixture of mineral oil and candle wax. The parts produced with the coated mold surface appeared to be more smooth and oily.

[0036] In a third case, commercially available polyester film was used to wrap the Run#1 sheet before thermoforming. It was very difficult to keep the

polyester film in pace during heating and thermoforming. But the region where the polyester film covered HDPE, appeared to be more shinny.

[0037] The parts, which were produced without coating the mold surface, were identified as "A", and the parts which were produced after coating the mold surface with 50:50 (wt.) mineral oil: candle wax, were identified as "B". Therefore, for example, part 4B would refer to material as in run#4 in table 1 or 2, produced with coated mold surface.

[0038] Since only the bottom of the part was contacting the mold surface, the anti-graffiti test was conducted on tray bottom only.

[0039] VI. Anti-Graffiti Test on the Thermoformed Trays:

[0040] The anti-graffiti test was conducted the same way as in *IV*. From the experimental result, it appears that the anti-graffiti properties appear to improve with increasing wax concentration. Tray #1A, which had no wax, did not pass the anti-graffiti test. Tray# 4A and 7A passed the test. The other trays were in between. The test results were the same for both waxes.

[0041] Trays # 1B through # 7B performed same as the corresponding extruded sheets. As mentioned above, the mold surface was coated with 50:50 blend of candle wax and mineral oil.

[0042] VII. Conclusions:

[0043] It appears that increasing wax concentration makes the thermoformed HDPE part better graffiti proof. Maximum wax concentration used under this contract was 1 percent. Improved anti-graffiti performance would be anticipated with higher amount of mineral oil and/or wax (1 ppm or higher up to 10%) based on the earlier data on mineral oil alone.

[0044] Coating the mold surface with a mixture of mineral oil and wax appears to be a viable avenue for the production of graffiti proof HDPE parts.

[0045] Any hydrocarbon, hydrocarbon mixture, modified hydrocarbon, modified hydrocarbon mixture, substituted hydrocarbon, substituted hydrocarbon mixture or any combination thereof, having solidification and/or melting point below 70 °C, preferably having melting point between 25-65°C, most preferably between 35-50C, when added at a concentration between 1 ppm and 10% by weight, preferable concentration between 1 ppm and 5%, to a polymer, preferably olefinic polymer, substituted olefinic polymer, modified olefinic polymer would provide anti-graffiti surface property. Similar anti-graffiti property can also be achieved by coating the mold surface with any of the mentioned additive prior to forming.

[0046] The anti-graffiti properties as described herein are also achievable by co-extruding or co-injection molding process, where the formulation described herein is used as a skin layer.

[0047] As any person skilled in the art of anti-graffiti compositions for a polymeric article will recognize from the previous detailed description, modifications and changes can be made to the preferred embodiments of the invention without departing from the scope of this invention.